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**Abstract**
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**Disciplines**
Physics | Quantum Physics

# van der Waals interactions in cholesteric liquid crystals

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Microscopic calculations of the pitch of cholesteric liquid crystals are based on a few types of interactions between molecules: (1) short-range repulsive, (2) direct Coulomb, and (3) long-range van der Waals interactions. Recently, it was shown that first two types cannot be treated in the frame of mean-field approximation. Here we show that, contrary to common belief, an accurate evaluation of the intermolecular dispersion forces contributing to chiral ordering requires consideration of biaxial correlations between molecules which are neglected in the mean-field approximation. We found that in the presence of biaxial correlations chiral interactions depend very weakly on the anisotropy of the local (i.e., atomic) polarizability. Instead, the chiral interaction between two molecules is dominated by the character of biaxial correlations, the isotropic part of local polarizability of one molecule, and a chiral parameter of the other molecule, which characterizes the chiral molecular geometry and is similar to that found previously for steric interactions.

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## I. INTRODUCTION

It is well known that liquids consisting of long rodlike molecules give rise to liquid crystalline phases [1]. In the nematic liquid-crystal phase these elongated molecules are preferentially aligned along a symmetry axis specified by the unit vector **n**, even though their centers of mass show no long-range order. In this paper, we wish to study the microscopic interactions that give rise to the cholesteric liquid crystal (CLC) phase, in which the local director **n(r)** describes a macroscopically helical structure with

$$\mathbf{n}(\mathbf{r}) = \hat{\mathbf{k}} \cos Qx - \hat{\mathbf{j}} \sin Qx, \tag{1}$$

where the axis of the helical structure (which is perpendicular to **n**) is arbitrarily assigned to the $x$ direction and $Q$ is the macroscopic chiral wave vector, defined so that a right-handed structure has $Q$ positive. In physically realizable systems, the chiral pitch, $P = 2\pi/Q$, is much larger than the intermolecular separation, in which case this phase, although chiral on large length scales, is locally identical to a nematic. We, therefore, will refer to this phase as the cholesteric nematic (CN) phase. It is known that one gets a CN phase if, and only if, some (or all) of the constituent molecules are chiral. (A chiral molecule is one that cannot be rotated into its mirror image [2]. For a discussion of chiral molecular symmetry see a recent review [3].) The terminology CN emphasizes the fact that a meaningful calculation of the macroscopic chiral wave vector $Q$ need only be carried out to leading order in the molecular chirality [4]. In particular, this implies that long-range biaxial order, which is an inescapable consequence of chiral ordering (since the chiral wave vector breaks the symmetry in the plane perpendicular to **n**), need only be considered if one is dealing with a system that would have long-range biaxial order in the absence of chiral interactions. In the situation we consider, the chiral wave vector is a consequence of ''turning on'' chiral interactions in an otherwise nematic liquid crystal that has only short-range biaxial order.

Up to now no consensus has been reached as to exactly which microscopic interaction between molecules dominates in producing the CLC phase. Among the interactions that have been invoked are [5]: (1) long-range attractive dispersion (van der Waals) interactions, (2) short-range repulsive interactions whose origin is in the Pauli principle (also called steric), and (3) direct Coulomb interactions which usually take the form of dipole–quadrupole interactions between electrically neutral mesogens. The latter two types can be interpreted as central force interactions between pairs of atoms or mass points on different molecules. Traditionally, the direct Coulomb interactions are ignored and can be a subject of future investigation. In contrast, the dispersion interaction is not equivalent to a classical two-body interaction. The distinction between two-body and many-body (i.e., dispersion) interactions, is that two-body interactions are known [6] to give $Q = 0$ when the orientation of each molecule is independently averaged over a distribution function that has the cylindrical symmetry of the nematic phase. In other words, within mean field theory, two-body interactions must give $Q = 0$. Thus, for two-body interactions a nonzero value of $Q$ can only be obtained when biaxial correlations between neighboring nematogens are explicitly taken into account [4]. In contrast, from the early calculations of van der Meer *et al.* [7] and Kats [8] it is clear that dispersion interactions do give a nonzero value of $Q$ even within mean-field theory. This has led, it seems, to the belief that for dispersion interactions it is not necessary to consider the role of orientational correlations between molecules. In this paper, we show that this is *not* the case.

Until recently, the calculations [7,8] have yielded formal expressions that can hardly be used to obtain order of magnitude estimates of $Q$. The resulting expressions for $Q$ involved molecular polarizabilities, which were not easy to estimate. In addition, the treatment was itself based on a

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multipole expansion whose use is questionable when applied to elongated nematogenic molecules. To overcome these objections we [9] recently carried out a numerical evaluation of the cholesteric pitch resulting from van der Waals intermolecular interactions when, as was customary, biaxial correlations were neglected. We used a modification of the multipole expansion in which only the transverse coordinates were treated perturbatively. This approach allowed us to treat a system of elongated molecules with intermolecular separation close to that observed in the real cholesteric. In this treatment, we also introduced a model in which the important excited states that determine the dispersion interaction were *p* states localized on each atomic site. It was found that the cholesteric pitch resulting from this model was usually much longer than that observed experimentally. A similar evaluation was done numerically for poly-gamma-benzyl-L-glutamate (PBLG) diluted in dioxane [10]. This evaluation showed that the cholesteric pitch arising from quantum interactions treated within the mean-field approximation was about 20 times longer than that found experimentally.

In this paper, on the basis of results obtained for the CLC consisting of DNA-like molecules, we claim that, similar to short-range repulsive interactions, the contribution of dispersion intermolecular forces to the chiral order cannot be evaluated reliably when orientational correlations between molecules are ignored. One illustration of this statement is provided by a treatment of a CLC consisting of polymers PBLG diluted in dioxane [10], where it was shown that a consideration of intermolecular biaxial correlations can give the cholesteric pitch comparable to the experimentally observed value. Thus, it is important for understanding chiral properties of PBLG liquid crystals to know the biaxial correlations, which were traditionally disregarded in treatments of this CLC [11–13].

When the dispersion chiral interactions between two molecules are considered in the mean field approximation, it was found [7,8] that the resulting effective chiral interaction could be expressed in terms of polarizabilities characteristic of the molecule as a whole. In particular, this interaction energy was found to be proportional to the anisotropic part of polarizability of one molecule and a higher order (third rank tensor) molecular polarizability, called the gyrotropy, which describes the chiral properties of the other molecule. In Ref. [9] it was shown that when the electrons are well localized on their atomic sites and within the *p* state model, the molecular polarizability can be expressed in terms of the local atomic polarizabilities and the molecular gyrotropy can be expressed in terms of the local atomic polarizabilities and the positions of the atoms within the molecule.

When one goes beyond mean-field theory and takes biaxial correlations into account, the description in terms of local atomic properties is again quite convenient. In addition, in this case, it is necessary to consider the detailed behavior of the chiral interaction as a function of $\alpha_I$, which specifies the angle through which molecule $I$ is spun about its long axis. Our study of the $\alpha$ dependence of the interactions leads to two main results. First, the $\alpha$-dependent part of this interaction is, in general, far larger than its average over the $\alpha$'s. In this situation, it is obviously important to take account of the correlations between the $\alpha$'s of the interacting molecules. Our second result is that although the average of this interaction over the $\alpha$'s of the interacting molecules depends on the anisotropy of the polarizability, the $\alpha$-dependent part of this interaction for typical values of the molecular parameters depends only weakly on the anisotropic part of the local polarizability of the molecules. Therefore, we are led to consider the case when the local polarizability is isotropic and consequently that both the anisotropy of the polarizability and the gyrotropy vanish. It is then relevant to identify the parameters that determine the strength of the chiral intermolecular interaction. As we shall see, the molecular chirality is described, not by the gyrotropy, but rather by a third rank tensor similar to that encountered in the treatment of steric interactions [4]. The anisotropy of the polarizability (which appears in the mean-field analysis of chiral interactions) is now replaced by the anisotropy associated with biaxial correlations in combination with the isotropic part of the polarizability. In view of the importance of biaxial correlations we give, in Appendix C, an analysis of the symmetry of these two molecule orientational correlation functions in the fully aligned nematic phase. We use this analysis to project out of our calculations $\alpha$-dependent contributions to the energy which do not survive averaging over orientational correlation functions consistent with local nematic symmetry.

Finally, we point out that a quantitative calculation of the cholesteric pitch of a system of helical molecules also requires a detailed knowledge of the distribution of the centers of neighboring molecules with respect to relative displacement along the local nematic director as well as the distribution of the lengths of constituent molecules. This implies that there is no universal, one-size fits all, theoretical explanation for the magnitudes of the chiral wave vector $Q$.

Briefly, this paper is organized as follows. In the following section, we will consider the pairwise interaction between molecules leading to the macroscopic chiral twist. This interaction will be treated within second-order perturbation theory. As we showed previously [9], macroscopic twist can arise from two distinct physical mechanisms: one in which both molecules are excited in the virtual state of two–molecule system and a second in which only one molecule is excited in the virtual state. The latter type of interaction appears important only in special cases since it requires the presence of local dipole moments arranged in the chiral order on one of the molecules rather than gyrotropy, which is characteristic for a two-molecule term. These cases are treated in Secs. II B and II C, respectively. Finally, in Sec. III we list our conclusions and briefly discuss the significance of our findings. The symmetry of the two-molecule orientational correlation function for a fully aligned nematic is discussed in Appendix C.

## II. EXACT EVALUATION OF CHIRAL QUANTUM INTERACTIONS

### A. Formulation

In this section, we analyze how van der Waals interactions give rise to the macroscopic chiral wave vector of cholesteric liquid crystals. We assume that each molecule has a small enough polarizability that we need consider only pairwise Coulomb interactions between molecules, which we treat quantum mechanically. Traditionally, the interaction potential between two molecules is expanded either with re-

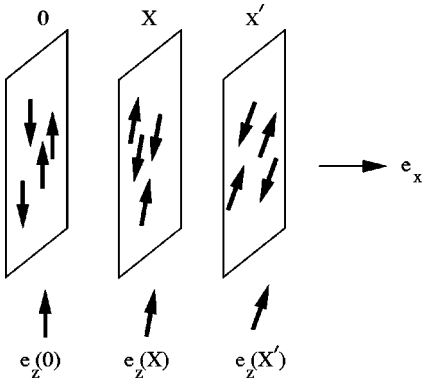


FIG. 1. The space fixed axes $\mathbf{e}_\mu$ in a CN. Here $\mathbf{e}_x$ is defined to lie along the cholesteric wave vector. We show the arrangement of molecules in planes perpendicular to $\mathbf{e}_x$ at $\mathbf{R}_x=0$, $X$, $X'$. The local director lies in the plane at $X$ is denoted $\mathbf{e}_z(X)$. The axis $\mathbf{e}_y(X)$ is such as to form the third member of a right-handed triad. For the plane at $\mathbf{X}$ the axis $\mathbf{e}_z(X)$ is rotated through an angle $\psi(R_x)=QR_x$ relative to $\mathbf{e}_z(0)$.

spect to all coordinates of charges on each molecule [14,7,8] or with respect to only their transverse coordinates with an assumption that molecules have elongated shapes [9,10]. In our treatment, we will evaluate the potential of interaction between molecules exactly, that is without making an expansion with respect to any coordinates of the charges on a molecule. This approach will require a numerical treatment of the problem, which in turn will necessitate a detailed model of each molecular constituent of the CLC. For simplicity, in our treatment we consider only a CLC consisting of identical chiral molecules, each of which has a helical shape. We will also assume the molecular wave functions to be strongly localized to the individual atoms. This assumption is valid in either of two scenarios. The first is if the bandwidth of the manifold of excited states is small compared to their average energy relative to the ground state. The second is if states are strongly localized by inhomogeneity. We will neglect thermal fluctuations assuming that there is a perfect alignment of the molecules either parallel to or antiparallel to the local nematic directors in the system. Thus it is necessary to specify a scalar variable, $\sigma\equiv\pm1$, which tells which way the molecule points and an angle variable, $\alpha$, which specifies the angle through which the molecule is spun about its long axis.

To carry out the calculations we will refer to three coordinate systems. In the space-fixed coordinate system, shown in Fig. 1, we introduce an axis $\mathbf{e}_x$ which coincides with the cholesteric wave vector $\mathbf{Q}$ as in Eq. (1). Also we take $\mathbf{e}_z(\mathbf{R})$ to be the axis along which the long axes of the molecules at $\mathbf{R}$ are perfectly aligned. The third local axis at $\mathbf{R}$ is chosen to form a right-handed coordinate system. For small $R_x$, $\mathbf{n}(R_x)$ will be rotated through a small angle $\psi(R_x)$ from its value at $R_x=0$. Thus to first order in $\psi$ we write

$$\mathbf{e}_x(\mathbf{R})=\mathbf{e}_x,$$

$$\mathbf{e}_y(\mathbf{R})=\mathbf{e}_y+\psi(R_x)\mathbf{e}_z, \tag{2}$$

$$\mathbf{e}_z(\mathbf{R})=\mathbf{e}_z-\psi(R_x)\mathbf{e}_y,$$

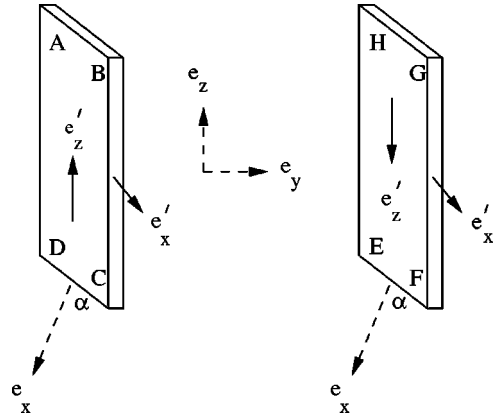


FIG. 2. The transformation of Eq. (3) from the space-fixed to the molecule-fixed axes, $\mathbf{e}'_\mu$. This molecule has points labeled $A$, $B$, $C$, and $D$ on one of its sides and on the other side it has points labeled $E$, $F$, $G$, and $H$, such that rotation by 180° about $\mathbf{e}_z$ takes $(A,B,C,D)$ into $(F,E,H,G)$. At the left we show the orientation of the molecule described by $\sigma=+1$ and $\alpha$ and at the right we show the molecular orientation for a molecule with $\sigma=-1$ and $\alpha$.

where $\mathbf{e}_\mu\equiv\mathbf{e}_\mu(0)$. The second coordinate system, shown in Fig. 2, is defined by the principal axes [15] $\mathbf{e}'_{x,I}$, $\mathbf{e}'_{y,I}$, and $\mathbf{e}'_{z,I}$ emblazoned on the $I$th molecule. Because we assume perfect alignment of the long axes, we have

$$\mathbf{e}'_{z,I}=\sigma_I\mathbf{e}_z,$$

$$\mathbf{e}'_{x,I}=\mathbf{e}_x\cos\alpha_I+\mathbf{e}_y\sin\alpha_I, \tag{3}$$

$$\mathbf{e}'_{y,I}=\sigma_I[\mathbf{e}_y\cos\alpha_I-\mathbf{e}_x\sin\alpha_I].$$

Note that rotation about the body axis $\mathbf{e}'_x$, takes $\sigma_I$ into $-\sigma_I$ and rotation about the body axis $\mathbf{e}'_y$ takes $(\sigma_I,\alpha_I)$ into $(-\sigma_I,\alpha_I+\pi)$. Finally, one has local axes $\mathbf{e}''_{\mu,i}$ for each atom $i$ on molecule $I$. Using the repeated index summation convention, we write

$$e''_{\mu,i}=O^{(i)}_{\mu\nu}e'_{\nu,I}, \tag{4}$$

where $\mathbf{O}$ is an orthogonal matrix and similarly for atom $j$ on molecule $J$. Components of a vector $\mathbf{r}$ with respect to these various systems are defined by

$$\mathbf{r}=r_\mu\mathbf{e}_\mu=r'_\mu\mathbf{e}'_\mu=r''_\mu\mathbf{e}''_\mu. \tag{5}$$

We now consider the interaction between two molecules $I$ and $J$ in the CN, where molecule $I$ is at the origin and molecule $J$ is at displacement $\mathbf{R}_{IJ}\equiv\mathbf{R}$. Because the twist angle between neighboring molecules is small, we will assume that the properties of this system are the same as those of the locally identical nematic system. Within this assumption [16], we refer all coordinates to the space-fixed axes that rotate slowly as a function of $R_x$ as shown in Fig. 1. Since the cholesteric wave vector $\mathbf{Q}$ lies along the space-fixed $x$ axis, the long axis of molecules $J$ is rotated with respect to that of molecule $I$ by a small angle $\psi(R_x)$ in the $\mathbf{e}_y$-$\mathbf{e}_z$ plane. The interaction Hamiltonian that arises from the Coulomb interaction between the $i$th charge on molecule $I$ denoted $q_i$, and its counterpart $q_j$ on molecule $J$ is given by

$$\mathcal{H}_{IJ}=\sum_{i\in I}\sum_{j\in J}\frac{q_i q_j}{|\mathbf{R}-\mathbf{r}_{ij}|}, \tag{6}$$

with $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, where $\mathbf{r}_i$ is the coordinate of the $i$th charge of molecule $I$ relative to the center of this molecule and similarly for $\mathbf{r}_j$. We now express $\mathbf{r}_j$ in terms of the space-fixed axes at molecule $J$:

$$\mathbf{r}_j=[\mathbf{r}_j\cdot\mathbf{e}_\beta(R_x)]\mathbf{e}_\beta(R_x), \tag{7}$$

where the space fixed axes at $R_x$ are related to those at the origin as

$$\mathbf{e}_\beta(R_x)=\mathbf{e}_\beta(0)-\psi(R_x)\epsilon_{x\alpha\beta}\mathbf{e}_\alpha(0), \tag{8}$$

where $\epsilon$ is the fully antisymmetric tensor, and, to be consistent with Eq. (1), $\psi(R_x)=QR_x$. Since the system is locally a nematic, we treat the coordinate $[\mathbf{r}_j\cdot\mathbf{e}_\beta(R_x)]\equiv r_{j,\beta}$ as in the untwisted nematic phase. Thus, we write

$$\mathbf{R}-\mathbf{r}_{ij}\equiv\mathbf{D}_{ij}=[\mathbf{R}-\mathbf{r}_{ij}]_\gamma\mathbf{e}_\gamma(0)-\psi(R_x)\epsilon_{x\alpha\beta}r_{j,\beta}\mathbf{e}_\alpha(0), \tag{9}$$

so that

$$\begin{aligned}D_{ij}&=|\mathbf{R}-\mathbf{r}_{ij}|\\&=[|\mathbf{R}-\mathbf{r}_{ij}|^2_{\psi=0}-2\{\epsilon_{x\alpha\beta}(\mathbf{R}-\mathbf{r}_i)_\alpha(\mathbf{r}_j)_\beta\}_{\psi=0}\psi(R_x)\\&\quad+O(\psi^2)]^{1/2},\end{aligned} \tag{10}$$

where the subscript $\psi=0$ means that the expression is evaluated in the absence of cholesteric twist. Throughout the rest of this paper this limit will be implicit. After substitution of Eq. (10) into Eq. (6) and expansion of $D_{ij}^{-1}$ with respect to $\psi$ one finds

$$\begin{aligned}\mathcal{H}_{IJ}=\sum_{i\in I}\sum_{j\in J}q_i q_j\left[\frac{1}{|\mathbf{R}-\mathbf{r}_{ij}|}+\psi(R_x)\frac{\epsilon_{x\alpha\beta}(\mathbf{R}-\mathbf{r}_i)_\alpha(\mathbf{r}_j)_\beta}{|\mathbf{R}-\mathbf{r}_{ij}|^3}\right]\\+O(\psi^2).\end{aligned} \tag{11}$$

We now consider an evaluation of the interaction energy between two molecules treating $\mathcal{H}_{IJ}$ via perturbation theory. In the first-order perturbation theory, the interaction energy is the ground-state expectation value of the Coulomb potential between atoms on different molecules. We will not analyze this interaction in the present paper. (This interaction is equivalent to a classical interaction, which can be treated as described elsewhere [4]). Here, we obtain the chiral interaction from $\mathcal{H}_{IJ}$ by evaluating the energy of interaction within second-order perturbation theory, whereby

$$E_{IJ}=-\sum_{n_I,n_J}{}'\frac{|(\mathcal{H}_{IJ})_{n_I,n_J;0,0}|^2}{E_{n_I n_J}}, \tag{12}$$

where the sums are over states $|n_I\rangle$ ($|n_J\rangle$) of molecule $I$ ($J$) and the prime indicates exclusion of the term when both molecules are in their ground state. Here, $E_{n_I n_J}$ is the energy (relative to the ground state) of the state when molecules $I$ and $J$ are in states $|n_I\rangle$ and $|n_J\rangle$, respectively. Then with help of Eq. (12) we can write the energy of interaction between two molecules giving the rise to their mutual twist leading to macroscopic chirality:

$$\begin{aligned}E_{IJ}=-2\psi(R_x)\sum_{ii'\in I}\sum_{jj'\in J}\sum_{n_I n_J}\frac{q_i q_{i'}q_j q_{j'}}{E_{n_I n_J}}\mathrm{Re}\{\langle 0|D_{ij}^{-1}|n_I n_J\rangle\\\times\langle n_I n_J|\epsilon_{x\alpha\beta}(\mathbf{R}-\mathbf{r}_{i'})_\alpha(\mathbf{r}_{j'})_\beta D_{i'j'}^{-3}|0\rangle\},\end{aligned} \tag{13}$$

where we only kept terms of order $\psi$.

The evaluation of the above expression leads to the consideration of two different situations: the first when in the virtual state $\{n_I n_J\}$ both molecules are excited (two-molecule case) and the second when in the virtual state only one molecule is excited (one-molecule case). The application of the approximation of local wave functions in both limits allows us to express the sum in Eq. (13) over excited states of the molecule $\{n_I\}$ in terms of a sum with $i'=i$ over the excited states $\{n_i\}_{i=1}^{N_a}$ of each atom. Accordingly, results will be expressed in terms of matrix elements within atoms or local complexes [9]. In so doing, it is natural to assume that the relevant excited state can be reached from the ground state by matrix elements of the dipole moment operator. In the numerical analyses below, we will consider only the contributions from the lowest $p$ orbitals of electrons on a molecule.

In order to calculate the macroscopic pitch $P$ from $E_{IJ}$ one must perform an average over the orientations and relative positions of the interacting molecules. Thus, we write $2\pi/P=h/K_2$, where $K_2$ is the Frank twist constant $h$ is the torque field [4], which we write as

$$\begin{aligned}h=-\frac{1}{2\Omega Q}\sum_{\sigma_I\sigma_J}\int_0^{2\pi}d\alpha_I\int_0^{2\pi}d\alpha_J\int d\mathbf{R}\,E_{IJ}(\alpha_I,\alpha_J;\mathbf{R})\\\times\hat{P}(\alpha_I,\sigma_I;\alpha_J,\sigma_J;\mathbf{R}),\end{aligned} \tag{14}$$

where $\hat{P}$ is the density of molecules at $\mathbf{R}$ with orientation specified by $\alpha_J$ and $\sigma_J$, given that there is a molecule at the origin with orientation specified by $\alpha_I$ and $\sigma_I$. When this equation is applied to a helical molecule, we may omit reference to the $\sigma$'s since molecule $I$ is invariant under change of sign of $\sigma_I$. In general, the average of Eq. (14) is a difficult one to perform. However, there is a number of simplifications, which are often made. For instance, within mean field theory, one neglects the correlations between the orientations of the two molecules. Thus, within mean-field theory we decouple the density $\hat{P}$ into the orientational distribution function $p_\alpha(\alpha,\sigma)$ of each molecule

$$\hat{P}(\alpha_I,\sigma_I;\alpha_J,\sigma_J;\mathbf{R}_{IJ})=\gamma p_\alpha(\alpha_I,\sigma_I)p_\alpha(\alpha_J,\sigma_J)f(\mathbf{R}_{IJ}), \tag{15}$$

where $\gamma$ is the number of nearest neighbors and the density of probability for location of molecule $J$, $f(\mathbf{R}_{IJ})$ has most of its weight at $(R_{IJ})_z=0$ and at the average intermolecular separation. Also in Eq. (15) the symmetry of the nematic phase implies that $p_\alpha(\alpha_I,\sigma_I)=(4\pi)^{-1}$. In what follows the mean field average of Eq. (14) is denoted by $\langle\ \rangle$, so that

$$P=-2\pi K_2\left[\left\langle\frac{E_{IJ}}{2Q\Omega}\right\rangle\gamma\right]^{-1}, \tag{16}$$

where here and in the following we take the volume per molecule to be $\Omega=LR^2$, $K_2=10^{-7}$ dyne and the number of nearest neighbors of a molecule $\gamma=6$.

The main point of this paper is to discuss the effect on the pitch of relaxing the mean-field constraint on the distribution function. In that case, we need to know something about the orientational distribution function. A simple ansatz is to assume that the position dependence of $\hat{P}$ can be decoupled from its dependence on molecular orientations. This dependence will be defined by the orientational distribution function $P_\alpha(\alpha_I,\sigma_I;\alpha_J,\sigma_J)$. In the case of purely steric interactions it was shown [4] that as long as the nematic order is reasonably well developed, the pitch can be calculated by convoluting the chiral contribution to $E_{IJ}$ with the nematic contributions to $P_\alpha$. In other words, it suffices to replace the orientational distribution function by its value when the molecular chirality has been turned off. We will invoke this approximation here. Accordingly, we need to know what the most general form is for $P_\alpha$ in a nematic. This question is addressed in Appendix C, where we show that in a nematic the most general form for the distribution function $P_\alpha$ for two molecules whose displacement is parallel to the twist wave vector $\mathbf{Q}$ (in the limit when the long axes are perfectly aligned) is

$$P_\alpha(\alpha_I,\sigma_I;\alpha_J,\sigma_J)=\sum_{k\not mn}[C(R^2)_{k\not mn}+D(R^2)_{k\not mn}\sigma_I\sigma_J]\times(\sin\alpha_I)^k(\sin\alpha_J)^{\not}(\cos\alpha_I)^m(\cos\alpha_J)^n, \tag{17}$$

where $k+\not$ and $m+n$ are even. The constraint that $k+\not$ is even is a result of assuming all molecules to be identical, while $m+n$ being even is a consequence of nematic symmetry. It follows from these constraints that only that part of $E_{IJ}$ which is invariant when the signs of both $\cos\alpha_I$ and $\cos\alpha_J$ are changed survives the average over a nematic symmetry distribution function $P_\alpha$. Accordingly, the assumption of nematic symmetry correlations indicates that we should replace $E_{IJ}$ by its component consistent with local nematic order:

$$E_{IJ}\to\tfrac{1}{2}[E_{IJ}(\alpha_I,\sigma_I;\alpha_J,\sigma_J)+E_{IJ}(\pi-\alpha_I,\sigma_I;\pi-\alpha_J,\sigma_J)]. \tag{18}$$

Finally we remark that, as follows from Appendix C, the given replacement is redundant when the displacement between two molecules is $\mathbf{R}=(R,0,0)$ and their orientations are identical: $\alpha_I=\alpha_I=0$. This fact will be used later.

### B. Two-molecule term

In the limit when both molecules are excited in the virtual state of two molecules one finds the following contribution into Eq. (13)

TABLE I. ''Default'' values of parameters used in the numerical evaluations. Only values used, which differ from those listed in this table will be given.

| $R$ | $L$ | $q$ | $a$ | $N_a$ | $E$ | $a_a$ | $\delta$ | $\eta$ | $K_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 20 Å | 200 Å | 0.4 Å$^{-1}$ | 7.5 Å | 200 | 8 eV | 1 Å | 0.2 | 0 | $10^{-7}$ dyne |

$$E_{IJ}^{(2)}=-2\psi(R_x)\,e^4\sum_{ij}\sum_{\mu\nu}E^{-1}_{i\mu;j\nu}\langle 0|D_{ij}^{-1}|i,\mu;j,\nu\rangle\times\langle i,\mu;j,\nu|\epsilon_{x\alpha\beta}(\mathbf{R}-\mathbf{r}_i)_\alpha(\mathbf{r}_j)_\beta D_{ij}^{-3}|0\rangle, \tag{19}$$

where $\mu$ and $\nu$ label excited $p$ states of atoms $i$ and $j$, respectively. (These states are assumed to be the real states $p_{x''}$, $p_{y''}$, and $p_{z''}$ referred to the local atomic axes.) For simplicity, we will always assume that $E_{i\mu;j\nu}$ is independent of locations of $i$ and $j$ atomic sites on the corresponding molecules. The above matrix elements can be expressed as

$$\langle 0|F(\mathbf{R},\mathbf{r}_i,\mathbf{r}_j)|i,\mu;j,\nu\rangle=\langle i,\mu|\Delta r''_{i,\mu}|0\rangle\langle j,\nu|\Delta r''_{j,\nu}|0\rangle\times\frac{\partial^2}{\partial r''_{i,\mu}\partial r''_{j,\nu}}F(\mathbf{R},\mathbf{r}_i,\mathbf{r}_j)\big|_{\mathbf{r}_i=\overline{\mathbf{r}}_i,\,\mathbf{r}_j=\overline{\mathbf{r}}_j}), \tag{20}$$

where $\Delta\mathbf{r}_i$ defines the location of $i$ electron with respect to the center of the $i$th atom on the $I$ molecule, $\overline{\mathbf{r}_i}$ is the expectation value of $\mathbf{r}_i$ in the ground state, i.e., the center of the atom associated with charge $i$. In Appendix A, we derive the expression for $E_{IJ}^{(2)}$ as a function of the orientations of the two interacting molecules.

For the purpose of numerical evaluation of the given interaction we introduce helical molecules identical to those considered in Ref. [9] where, unless otherwise specified, the length of a molecule $L$, the molecule wave number $q$, the radius of the molecular helix $a$ and other parameters are given in Table I. The position components of the $i$th atom in the molecule-fixed coordinate system are

$$z'_i=s_i,\ x'_i=a\cos(qs_i),\ y'_i=a\sin(qs_i), \tag{21}$$

where the $s_i=[-\frac{1}{2}+(i-1)/(N_a-1)]L$ for $i=1,2,\ldots,N_a$, where $N_a$ is the number of atoms in a molecule. With appropriate relabeling, the space-fixed locations of the atoms may be taken to be

$$x_i=a\cos(qz_i+\alpha_I),\quad y_i=a\sin(qz_i+\alpha_I),\quad z_i/L=-\tfrac{1}{2}+(i-1)/(N_a-1). \tag{22}$$

This result displays explicitly the symmetry of the helix with respect to $\sigma_I\to-\sigma_I$ corresponding to the twofold rotation axis. (The orientational distribution functions are thus independent of the $\sigma$'s.) The locally defined principal axes for the $i$th atom are chosen in the way shown in Fig. 3. It is convenient to write them as

$$\mathbf{e}''_x=\mathbf{e}_x\cos(qz_i+\alpha_I)+\mathbf{e}_y\sin(qz_i+\alpha_I),$$

$$\mathbf{e}''_y=-\mathbf{e}_x c\,\sin(qz_i+\alpha_I)+\mathbf{e}_z c\,\cos(qz_i+\alpha_I)\mathbf{e}_y-caq,$$

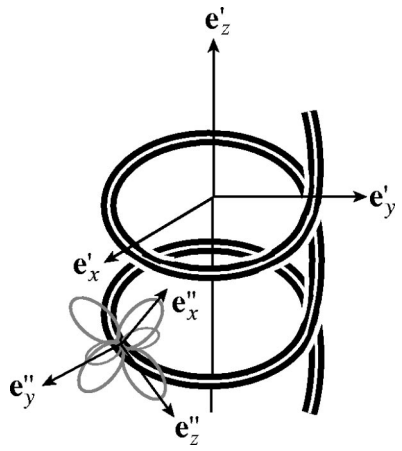


FIG. 3. Local atomic coordinate system, defined by the unit vectors $\mathbf{e}''_\mu$, showing that the local excited $p$ states define the orientation of the local axes. Here, $\mathbf{e}''_z$ is the unit vector tangent to the helix, the unit normal, $\mathbf{e}''_x$, lies along the radius of curvature, and the binormal unit vector $\mathbf{e}''_y$ is the third member of the triad of mutually perpendicular unit vectors.

$$\mathbf{e}''_z = -\mathbf{e}_x caq\ \sin(qz_i+\alpha_I)+\mathbf{e}_z caq\ \cos(qz_i+\alpha_I)\mathbf{e}_y+c, \tag{23}$$

where $c^2=[1+(aq)^2)]^{-1}$. Here, $\mathbf{e}''_z$ is the tangent vector to the helix, $\mathbf{e}''_x$ is a unit vector along the radius of curvature, and $\mathbf{e}''_y$ is the unit vector along the binormal or the third orthogonal direction.

We will set the matrix elements $\langle i,\mu|\Delta r''_{i,\mu}|0\rangle$ and $\langle j,\nu|\Delta r''_{j,\nu}|0\rangle$ equal to $a_a=1$ Å and characterize the anisotropy of the atomic polarizability through the relations

$$E_{x''}/E=1+\frac{1}{3}\delta+\eta, \quad E_{y''}/E=1+\frac{1}{3}\delta-\eta,$$

$$E_{z''}/E=1-\frac{2}{3}\delta, \tag{24}$$

where $E$ is the average excitation energy and $x''$, $y''$, $z''$ label the local principal axes of the atom. Within our assumption of constant matrix elements the parameters $\delta$ and $\eta$ characterize the anisotropy of the excitation energy and through it the anisotropy of the atomic polarizability. For a molecule with an anisotropic polarizability we will set: $E=8$ eV, $\delta=0.2$, and $\eta=0$, so that the local polarizability tensor has its largest component along the tangent to the helix, as one would expect physically.

First, we evaluate the dispersion interaction in the mean-field approximation with given Frank twist constant $K_2$. After finding $E_{IJ}^{(2)}/Q$ from Appendix A we will average this ratio with respect to positions of nearest neighbors of $I$ molecule, which are located at random on its equatorial circumference of radius $R$, as described in connection with Eq. (16). As mentioned, we neglect any correlations between positions of molecules and independently spin each of them. We remark here that numerically spinning of the molecules at small separations should be performed very accurately, i.e., over a large number of molecular orientations $\alpha$ in its equatorial plane. In evaluating $E_{IJ}^{(2)}/Q$, we first consider the case

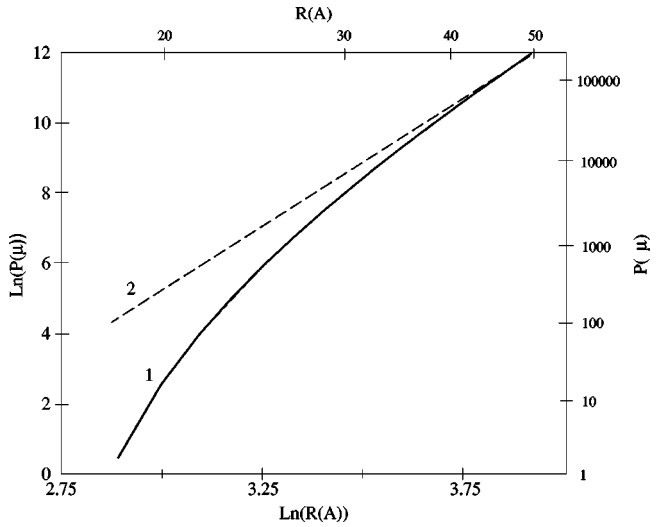


FIG. 4. Cholesteric pitch as a function of separation $R$ between helical molecules. Results are for the parameter values of Table I. The solid line is from an exact numerical evaluation of $E_{IJ}^{(2)}$ from the present paper, as described in Appendix A. The dashed line is from Ref. [9] and is based on the analytic expansion in powers of transverse coordinates.

of isotropic polarizability, $\delta=\eta=0$. For this case, it is known that within the multipole expansion [7,8] or modified multipole expansion [9], mean-field theory gives $\langle E_{IJ}\rangle=0$. However, we expect that this result does not depend on the validity of such expansions. Indeed, in confirmation of this idea, our numerical work gave $\langle E_{IJ}^{(2)}\rangle=0$. Second, in Fig. 4 we show how the mean-field result for the cholesteric pitch depends on the intermolecular separation for $\delta=0.2$ and $\eta=0$. It follows that the modified multipole expansion of the interaction potential used in Ref. [9] is not accurate at very small intermolecular distances. This expansion works well down to a separation $\approx$35 Å, which corresponds to $\sim$15% of the molecule volume density $\xi$ approximately given by $(2\pi a^2)/(\sqrt{3}R^2)$. We now discuss how the cholesteric pitch $\sim 2\,\mu$m we found at $R=18$ Å (volume density $\approx$60%) compares with what one would expect in view of experiments. One must realize that at this separation the distance between closest interacting atoms is only 3 Å, that our molecules are very chiral instead of having only a few chiral centers, that atomic polarizability we used is rather high and the Frank twist constant is rather low. Thus, our result should be compared to the minimum observed pitch that is found to be at most a fraction of a micron [1]. So we expect that the dispersion interaction between molecules treated within the mean-field approximation can make a significant contribution to the chiral order only in the very special cases.

Now let us estimate the role of biaxial correlations for the dispersion forces contributing into the chiral intermolecular interactions. For this purpose, we will evaluate the energy of chiral interaction $E_{IJ}^{(2)}$ as a function of $\alpha_I$ and $\alpha_J$ for the case when $\mathbf{R}$ is in the same direction as $\mathbf{Q}$, which we indicate by the notation $\mathbf{R}\uparrow\uparrow\mathbf{Q}$. Figures 5(a) and 5(b) show the value of $E_{IJ}^{(2)}/2Q$ and its component, which is consistent with local nematic order [as defined in Eq. (18)], respectively. On each plot the $I$th molecule has four different equatorial orientations given by $\alpha_I=0°$, 90°, 180°, and 270°, while the $J$th

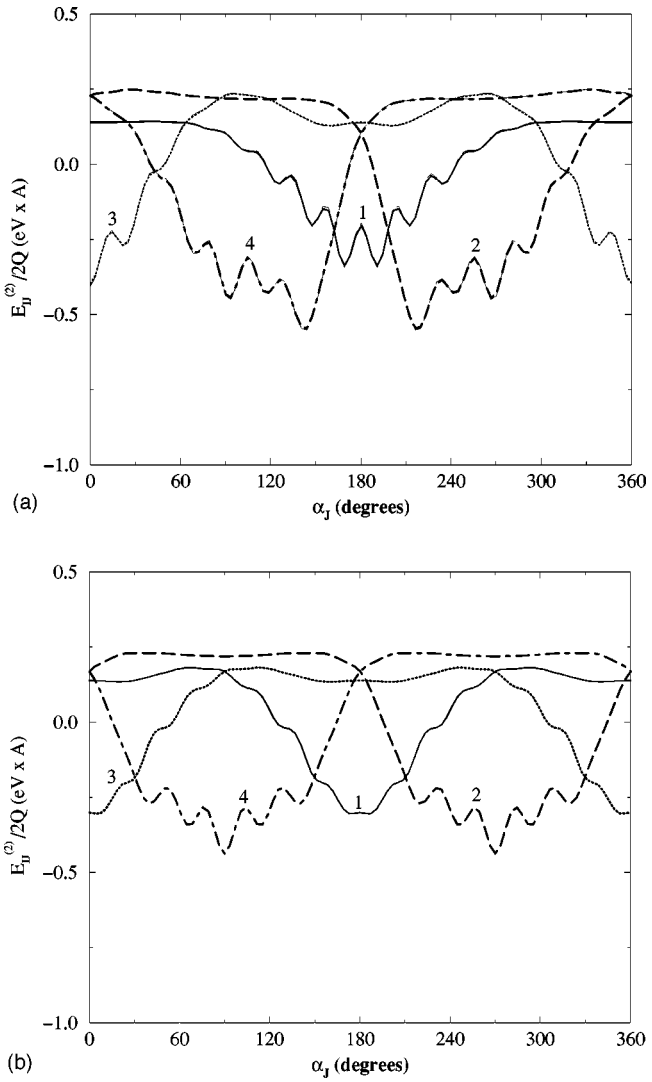


FIG. 5. The energy of interaction $E_{IJ}^{(2)}/2Q$ [panel (a)] and its component consistent with local nematic order [panel (b)] as a function of the equatorial rotation by angle $\alpha_J$ of the molecule $J$ at different angles $\alpha_I$ of molecule $I$: $\alpha_{I1}=0°$, $\alpha_{I2}=90°$, $\alpha_{I3}=180°$, $\alpha_{I4}=270°$, where the index of $\alpha$ corresponds to the number of the curve, and $\mathbf{R}\uparrow\uparrow\mathbf{Q}$. Each graph has two indistinguishable curves representing interaction between molecules with anisotropic and isotropic polarizabilities, that is when $\delta=0.2$, $\eta=0$, and $\delta=\eta=0$, respectively. The rest of parameter values are as in Table I.

molecule is rotated through an angle $\alpha_J \in [0°, 360°]$. (Note that the presence of local peaks is defined by the details of the molecule structure. As the density of atoms $\rho$ or separation between molecules increases these peaks are smoothed out). We see that at small intermolecular separation $E_{IJ}^{(2)}$ is dominated by its component consistent with local nematic order, though, as follows from Appendix V, this dominance disappears as the separation between molecules increases and so symmetrization defined by Eq. (18) becomes necessary. In Fig. 5, we observe that the $\alpha$-dependent contribution to $E_{IJ}^{(2)}/(2Q)$ has an amplitude of about 0.5 eV Å . If this energy is independently averaged over $\alpha_I$ and $\alpha_J$, as done in mean-field theory, the result would be $2\times10^{-4}$ eV Å corresponding to the cholesteric pitch $\approx 14$ $\mu$m. In other words, the angular dependent part of the interaction energy is about three orders of magnitude larger than its average obtained by spinning both molecules uniformly over all values of $\alpha$. This being the case, even small departures from a uniform distribution can have a profound effect on the calculated value of the macroscopic pitch. Clearly, we expect correlations between the orientations of adjacent molecules will be reflected by nonuniformity in the distribution of $\alpha$ values. Thus, we arrive at the situation that is similar to the one with central force interaction between atoms on two molecules where for the system to be chiral one has to invoke the intermolecular biaxial correlations. For dispersion forces even though we obtain nonzero chiral interactions within the mean-field approximation, the presence of biaxial correlations will increase them significantly. Thus, we conclude that biaxial correlations should always be taken into account.

In Fig. 5, we plot results for two cases, one in which local polarizability of a molecule is anisotropic ($\delta=0.2, \eta=0$) and another for which the polarizability is isotropic ($\delta=0, \eta=0$). Within the resolution of this figure one cannot distinguish between these two results. In contrast to the results of van der Meer and others [7–9] derived for $E_{IJ}^{(2)}/2Q$ in the mean-field approximation, we find that the orientational dependence of $E_{IJ}^{(2)}$ is nearly independent of the anisotropic part of the local polarizability of a molecule in the presence of strong biaxial correlations. (From the analysis of Appendix VII, one can deduce that this statement cannot remain true when $a \ll R$. Although in practical cases this limit is probably not realized.)

The fact that we can get a finite pitch even when the polarizability is isotropic, raises a question as to what parameters set the scale for this interaction energy. As discussed in Ref. [3], the scale for the chiral energy of interaction is set by the product of a chiral parameter of one molecule times some achiral property, usually an anisotropy, of the second molecule. Within the mean field treatment of interactions in which $E^{(2)}$ is averaged over $\alpha$'s, it is known [7–9] that $E^{(2)}$ is proportional to the product of the molecular gyrotropy (which characterizes the molecular chirality in this case) and the anisotropy of the polarizability. However, since these parameters are both zero when $\delta=\eta=0$, the $\alpha$-dependent twist energy shown in Fig. 5 must be scaled by some different parameters. In order to identify appropriate parameters, we present an analysis in Appendix V for the case $\delta=\eta=0$. We find that now the chirality of a molecule is characterized by the third-rank tensor component, $\Sigma_i x_i' y_i' z_i'$, where these coordinates are taken relative to principal axes [15] of the molecule. Such a result is not surprising, because when the polarizability is isotropic, we are dealing with interactions that are not very different from steric interactions where just this type of chiral parameter has been shown to be relevant [4,3]. The quantity analogous to the anisotropy of the polarizability is harder to identify unambiguously. Clearly, we are invoking anisotropy due to biaxial correlations. Also, the result is proportional to the magnitude of the isotropic part of the polarizability. So here these two factors, in combination, play the role that the anisotropy of the polarizability plays in the mean field result.

We should note an unexpected result shown by Fig. 5 and corroborated by the analytic analysis given in Appendix D for the limit $a \ll R$: even in the large $L$ limit the energy $E_{IJ}^{(2)}$ is *not* simply a function of $(\alpha_1-\alpha_2)$. This energy contains

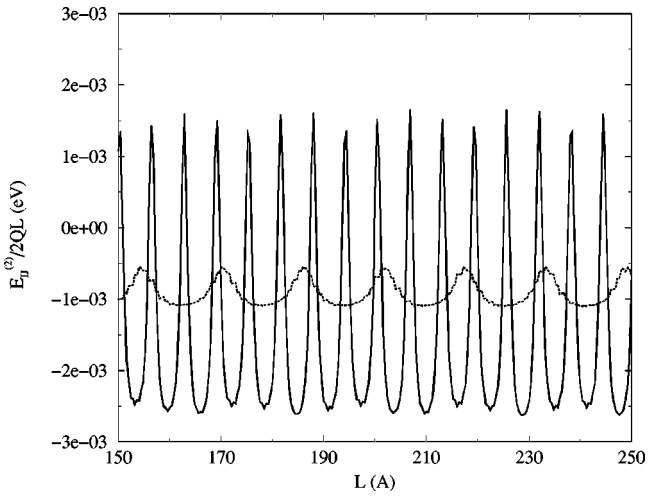


FIG. 6. The energy of chiral interaction $E_{IJ}^{(2)}/2QL$ between two molecules $I$ and $J$ ($\mathbf{R}\uparrow\uparrow\mathbf{Q}$) versus their molecular length $L$ when $\alpha_J=\alpha_I=0$ and the other parameters are in Table I, except for $q$ and $\rho$. The solid curve represents the two molecules with the wave number $q=1$ Å$^{-1}$ and linear density of atoms $\rho=2.5$ Å$^{-1}$ while the dashed curve represents the two molecules with $q=0.4$ and $\rho=1.0$ Å$^{-1}$.

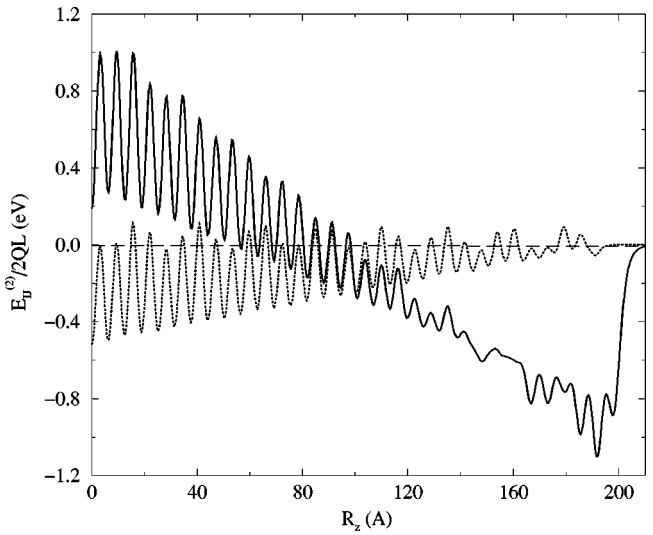


FIG. 7. The energy of chiral interaction $E_{IJ}^{(2)}/2QL$ between two molecules $I$ and $J$ ($\mathbf{R}_\perp\uparrow\uparrow\mathbf{Q}$) versus displacement $R_z$ of the center of $J$ molecule along its local nematic director when $\alpha_J=\alpha_I=0$. The solid curve corresponds to the system with molecules of the length 200.8 Å while the dotted curve is for one with molecular length 197.0 Å. In both cases, the molecule wave number is $q=1$ Å$^{-1}$ and the linear density of atoms is $\rho=2.5$ Å$^{-1}$, $R_\perp=20$ Å, and the other parameters are as in Table I.

terms proportional to $\cos(\alpha_1+\alpha_2)$ and to $\cos(2\alpha_1)+\cos(2\alpha_2)$. The appearance of such terms show that no matter how large $L$ is, end effects remain important.

Next we study the dependence of the chiral energy on the length $L$ of the molecules. Figure 6 reveals the oscillatory behavior of $E_{IJ}^{(2)}/2QL$ versus the length $L$ of identical molecules for two values of a molecule wave number: 0.4 and 1 Å$^{-1}$ when their orientations are given by angles $\alpha_I=\alpha_J=0$ and $\mathbf{R}=(R,0,0)$. The oscillations with the period proportional to the molecular pitch reflect end effects and the helical nature of the constituent molecules, as is analyzed in Appendix D. Figure 6 suggests that $E_{IJ}^{(2)}$ would have an oscillatory dependence on the relative displacement $R_z$ between two molecules along their long axis. To confirm this, we evaluated this energy as a function of $R_z$ in Fig. 7 for the special case when $\alpha_I=\alpha_J=0$, $\mathbf{R}_\perp=(R_\perp,0,0)$, the molecule wave number $q=1$ Å$^{-1}$, and both molecules have the lengths 197 or 200.8 Å. It follows that consideration of the distribution function of the displacement $R_z$ will reduce the effect of oscillations in $E_{IJ}^{(2)}$ with respect to the lengths of two molecules. We remark that these results suggest that if one constructs a system in which, to high accuracy, the constituent molecules all have the same length, $L$, then varying $L$ may cause a change of the sign of the torque field [17].

To study the role of orientational correlations between molecules, we construct the torque field [4], $h$ of the CLC as given in Eq. (14). In evaluating $h$ we will assume that the molecule at the origin has $\gamma$ neighbors at a displacement with $z$-component zero and magnitude $R_\perp$, but with $x$ and $y$ components random in direction. We estimate the effect of biaxial correlations by considering a few possible situations for the biaxial correlations between molecules:

(1) First we suppose that there is long-range biaxial order, so that locally each molecule is perfectly oriented in its equatorial plane at fixed angles $\alpha_I=\alpha_J=0$. Then the torque field is given by

$$h=-\frac{\gamma}{4\pi\Omega Q}\int_0^{2\pi}d\phi\,E_{IJ}(0,0;R_\perp\cos\phi,R_\perp\sin\phi,0). \tag{25}$$

(2) Second, we assume that although there is no long-range biaxial order, there are strong pairwise biaxial correlations between molecules, which forces two molecules to have the same orientation *relative to* $\mathbf{R}_\perp$ while the rest of the molecules are ignored. Equation (14) can be written as

$$h=-\frac{1}{4\pi\Omega Q}\int_0^{2\pi}d\phi\,E_{IJ}(\phi,\phi+\Delta;R_\perp\cos\phi,R_\perp\sin\phi,0), \tag{26}$$

where, for this case, $\Delta=0$. Thus, here both molecules have their body $x$-axis parallel to $\mathbf{R}_\perp$.

(3) Finally, we consider strong pairwise biaxial correlations (as in case 2, above) such that Eq. (26) holds with $\Delta=\pi/2$. In this case the body $x$ axis of one molecule is parallel to $\mathbf{R}_\perp$ and that of the other is perpendicular to $\mathbf{R}_\perp$.

The results for the torque field and cholesteric pitch as functions of average separation between molecules appearing in each of the above situations are depicted in Fig. 8. The graphs shown there represent the torque field of a CLC formed by chiral molecules with local anisotropic polarizability defined by $\delta=0.2$ and $\eta=0$. As expected, this torque field is indistinguishable from that of a CLC formed by molecules identical except with isotropic polarizability ($\delta=\eta=0$). The corresponding cholesteric pitch is shown when the Frank twist constant is equal to $10^{-7}$ dyne. From Fig. 8, it may be seen that as the correlations among molecules increase, the cholesteric pitch significantly decreases. In addi-

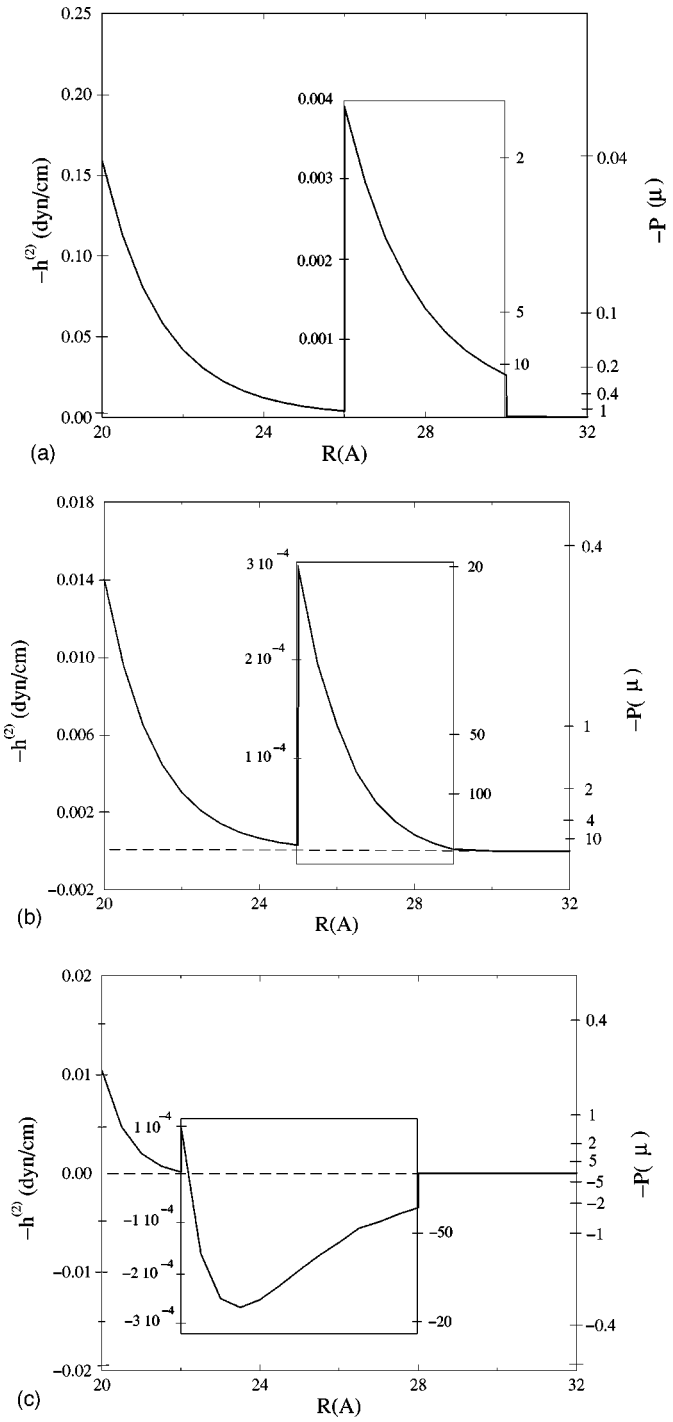


FIG. 8. The torque field $h$ as a function of the average intermolecular distance $R$ in the cases, discussed in the text, when (1) there is long-range biaxial order with $\alpha=0$ for all molecules, (2) there are strong pairwise biaxial correlations and $\alpha_J=\alpha_I=\phi$, (3) there are strong pairwise biaxial correlations between molecules and $\alpha_J=\alpha_I+\pi/2=\phi$. Each plot represents two indistinguishable curves for the two–molecule terms: one for $\delta=0.2, \eta=0$, and the other for $\delta=0, \eta=0$. The other parameters are as in Table I.

tion, we see that the chiral interaction is very sensitive to the details of the mutual biaxial orientations of molecules and, as a consequence, their knowledge is essential for accurate treatment of the problem.

### C. One-molecule term

As was shown in Ref. [9] a new type of interaction arises if only one molecule is excited in the virtual state of two-molecule system. In this case we derive the contribution to the energy of chiral interaction given by Eq. (13):

$$E_{IJ}^{(1)}=-2\psi(R_x)e^2\Bigg[\sum_{ii'\in I}\sum_{j\in J}\sum_{\nu} q_i q_{i'}|\langle j,\nu|\Delta r_{j,\nu}|0\rangle|^2 E_\nu^{-1} \times\Bigg\{\frac{\partial D_{ij}^{-1}}{\partial r''_{j,\nu}}\frac{\partial[\epsilon_{x\alpha\beta}(\mathbf{R}-\mathbf{r}_{i'})_\alpha(\mathbf{r}_j)_\beta D_{i'j}^{-3}]}{\partial r''_{j,\nu}}\Bigg\}_{\mathbf{r}_i=\bar{\mathbf{r}}_i,\mathbf{r}_{i'}=\bar{\mathbf{r}}_{i'}} +\Phi(I\Leftrightarrow J)\Bigg], \tag{27}$$

where $\Phi(I\Leftrightarrow J)$ designates the corresponding term when molecule $I$ is excited and molecule $J$ is in its ground state, and the summation over $i\,(i')$ includes both the charges of the electrons and the nuclei, whose positions are taken in the ground state. The sum over both signs of charge within an atom leads to the replacement

$$q_i\rightarrow \mathbf{d}_i\cdot\nabla_i, \tag{28}$$

where $\mathbf{d}_i$ is the dipole moment of atom $i$ and on the right-hand side of this equation the index $i$ now labels atoms rather than individual charges. Thus,

$$E_{IJ}^{(1)}=-2\psi(R_x)e^2\Bigg[\sum_{ii'j}\sum_{\mu\mu'\nu}|\langle j,\nu|\Delta r_{j,\nu}|0\rangle|^2 E_\nu^{-1} d_{i,\mu}d_{i',\mu'} \times\Bigg\{\frac{\partial^2 D_{ij}^{-1}}{\partial r''_{j,\nu}\partial r''_{i,\mu}}\frac{\partial^2[\epsilon_{x\alpha\beta}(\mathbf{R}-\mathbf{r}_{i'})_\alpha(\mathbf{r}_j)_\beta D_{i',j}^{-3}]}{\partial r''_{j,\nu}\partial r''_{i',\mu'}}\Bigg\}_{\mathbf{r}_i=\bar{\mathbf{r}}_i,\mathbf{r}_{i'}=\bar{\mathbf{r}}_{i'}} +\Phi(I\Leftrightarrow J)\Bigg]. \tag{29}$$

To estimate these chiral interactions between molecules, we again consider our model helical molecule. But now we attribute the local dipole moments of constant values to each molecule and arrange them consistent with the local symmetry:

$$\begin{aligned} d_x&=\sigma_I[d_{x''}\cos(qs+\alpha)-cd_{y''}\sin(qs+\alpha) -caqd_{z''}\sin(qs+\alpha)],\\ d_y&=\sigma_I[d_{x''}\sin(qs+\alpha)+cd_{y''}\cos(qs+\alpha) +caqd_{z''}\cos(qs+\alpha)],\\ d_z&=\sigma_I[-caqd_{y''}+cd_{z''}]. \end{aligned} \tag{30}$$

The detailed expression for $E_{IJ}^{(1)}$ is given in Appendix A. Note that because $E^{(1)}$ involves two dipole moments on the same molecule, it does not depend on how the dipoles on

different molecules are correlated. We pick the macroscopic and microscopic parameters of the system identical to those used in Sec. II B with the number of local dipole moments on each molecule equal to the number of atoms : $N_d = N_a = 200$, and the values of dipole moments $d_{x''} = ed$, $d_{y''} = d_{z''} = 0$.

First, similarly to the previous section, we will numerically evaluate the magnitude of the macroscopic pitch, within the scope of the mean field approximation. If molecules are spun independently then it turns out that at high volumetric density $\xi \approx 50\%$ ($R = 20$ Å) the macroscopic pitch is $P = 0.13\,(a_a/d)^2\,\mu m$. The resulting pitch is small enough to be relevant. However, as for the two–molecule term, the presence of biaxial correlations between molecules needs to be evaluated. Fig. 9 shows the one–molecule term $E_{IJ}^{(1)}(a_a/d)^2/(2Q)$ and its component consistent with local nematic symmetry of CN, as defined by Eq. (18). The two molecules $I$ and $J$ have locations such that $\mathbf{R}\uparrow\uparrow\mathbf{Q}$ and the $J$th molecule is rotated through the angle $\alpha_J \in [0^o, 360^o]$ for four fixed orientations of the $I$th molecule. As usual, we plot two curves: one for the case when interacting molecules have anisotropic polarizability given by $\delta = 0.2$, $\eta = 0$ and the other when the molecules are isotropic with $\delta = \eta = 0$. We observe that at separation 20 Å there is a noticeable difference between two curves, which indicates a strong chiral interaction in the mean-field approximation leading to a small cholesteric pitch. Nevertheless, the part of the energy of interaction that disappears when two molecules are independently spun has dominant contribution, which quickly becomes overwhelming as the intermolecular separation increases. The last statement is illustrated by Fig. 10, which reveals the one–molecule term $E_{IJ}^{(1)}(a_a/d)^2/2Q$ with $\delta = 0.2$, $\eta = 0$ and $\delta = \eta = 0$ versus separation $R$ when $\mathbf{R}\uparrow\uparrow\mathbf{Q}$ and $\alpha_I = \alpha_J = 0$. There the difference between two curves quickly decreases as separation growths. Accordingly, one expects that disregard of biaxial correlations between molecules leads to a significant overestimation of resulting cholesteric pitch. It follows that the anisotropy of the molecular polarizability and chirality of the dipole arrangement can be used in very rough estimation of the strength of chiral interaction at very small separation between molecules. As separation increases the effective interaction becomes dominated by the isotropic part of the polarizability of one molecule, the chirality of the arrangement of the dipoles on the other and the biaxial correlations between given molecules.

Similar to two-molecule term $E_{IJ}^{(1)}/2QL$ undergoes oscillations [10] as the length of each molecule is varied. This underlines the necessity of accurate knowledge of the energy $E_{IJ}^{(1)}$ versus the relative displacement $R_z$ between molecules.

Finally we point out that the cholesteric pitch rising from one–molecule type of interaction is proportional to $(a_a/d)^2\,(N_a/N_d)^2$. Because both ratios usually tend to be very small [in the above analysis we chose $(N_a/N_d) = 1$], we conclude that the considered interaction is significant only in special cases and usually can be neglected.

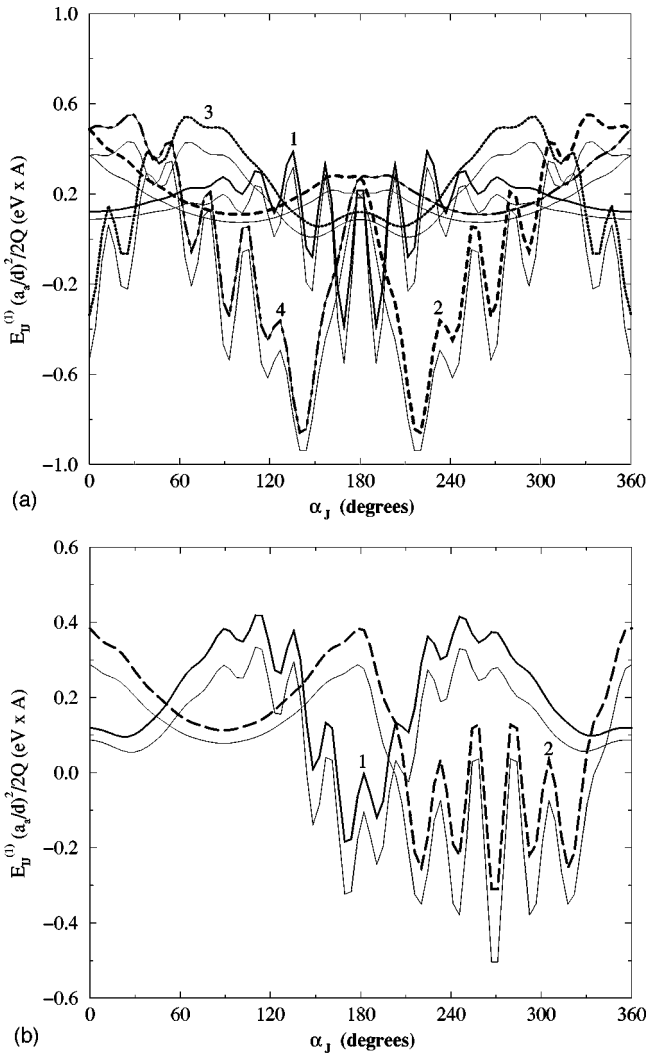


FIG. 9. The energy of interaction $E_{IJ}^{(1)}(a_a/d)^2/2Q$ [panel (a)] and its component consistent with local nematic order [panel (b)] as a function of the equatorial rotation $\alpha_J$ of the molecule $J$ at different angles $\alpha_I$ of molecule $I$: $\alpha_{I1} = 0°$, $\alpha_{I2} = 90°$, $\alpha_{I3} = 180°$, $\alpha_{I4} = 270°$, where the index of $\alpha$ corresponds to the number of the curve, and $\mathbf{R}\uparrow\uparrow\mathbf{Q}$. In panel (b) for clarity only graphs 1 and 2 are shown, the graphs 3 and 4 can be reconstructed by translation of the graphs 1 and 2 by the angle $\alpha_J = 180°$, respectively. Parameters, except for $\delta$, are taken as in Table I. Each graph has two parallel curves corresponding to the interaction of molecules with anisotropic polarizability (thick line): $\delta = 0.2, \eta = 0$, and isotropic polarizability (thin line): $\delta = 0, \eta = 0$.

## III. CONCLUSION

Here we record our conclusions and put our work into the context of current research.

(1) For CLC consisting of chiral molecules of helical shape (patterned after DNA) we found that the magnitude of cholesteric pitch $P$ rising from dispersion interactions between molecules evaluated within the mean-field approximation (in which biaxial correlations are neglected) but without any type of multipole expansion (as used heretofore) is shorter than found previously, but still is significantly longer than we expect from experimental data.

(2) Going beyond the mean-field approximation, we analyzed the effect of intermolecular biaxial correlations. It was found that, in contrast to the common belief, these correlations play a dominant role in the evaluation of the pitch $P$ arising from van der Waals interactions. In fact, the presence of biaxial correlations may lead to an increase in the chiral

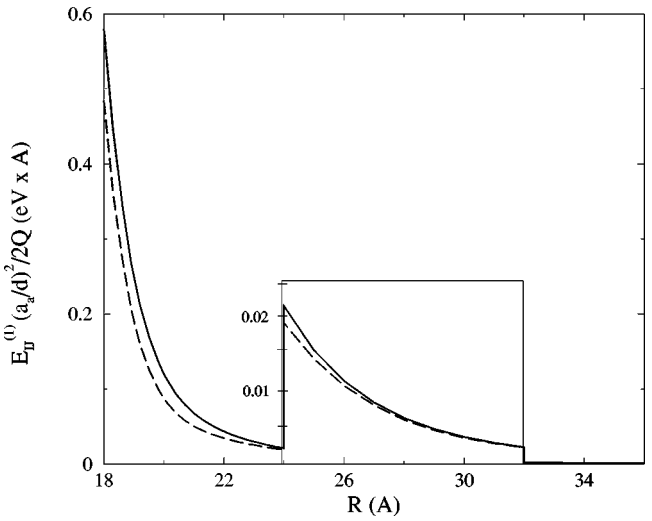


FIG. 10. The one–molecule term $E_{IJ}^{(1)}(a_a/d)^2/2Q$ when $\mathbf{R}\uparrow\uparrow\mathbf{Q}$ and $\alpha_J=\alpha_I=0$. The solid and dashed curves represent the cases when $\delta=0.2$, $\eta=0$ and $\delta=\eta=0$, respectively. Other parameters are as in Table I.

interaction by a few orders of magnitude in comparison to an effective interaction considered within the mean field approximation.

(3) In the presence of biaxial correlations we also found that for typical molecular parameters (in which the transverse dimension of the molecule is not very small compared to the intermolecular separation) the chiral interaction between molecules depends only very weakly on the anisotropic part of the molecular polarizability. This result contrasts with the known [7–9] fact that the chiral interaction between biaxial correlations are neglected is proportional to product of anisotropy of the polarizability and the gyrotropy (which itself requires an anisotropic polarizability). In the presence of biaxial correlations the pitch $P$ is determined by the chiral geometry of the molecules (similarly to the case of steric interactions [4]) and the combined effect of biaxial correlations and the isotropic part of the polarizability.

(4) We also gave (in Appendix C) an explicit construction of the allowed form of the two-particle orientational distribution function for achiral molecules in a fully aligned uniaxial nematic. This analysis pinpoints the types of correlations that are allowed in the limit when molecular chirality is ''turned off.'' We suggest that it is useful to eliminate from consideration terms in the interaction energy, which do not survive the average over the nematic symmetry distribution function, as we did in the results shown in Figs. 5 and 9. Since it now seems that both steric and quantum interactions are crucially affected by biaxial correlations, we hope that these correlations *in nematics* will be studied by simulation techniques.

(5) Our calculations can potentially be generalized in several directions. For instance, our analysis can be applied to a liquid crystal containing a mixture of chiral and achiral molecules. In addition, one can apply the approach used here to consider real chiral systems as was done elsewhere [10] for a CLC consisting of PBLG diluted in dioxane. We hope that the current work will stimulate numerical simulations of CLC's with inclusion of van der Waals interactions.


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## APPENDIX A: EXACT CHIRAL TERMS

To evaluate Eq. (19) we need matrix elements of two quantities. These are

$$F^{(1)}\equiv\frac{1}{|\mathbf{D}_{ij}|}=\frac{1}{|\mathbf{R}-\mathbf{r}_{ij}|} \tag{A1}$$

and

$$F^{(2)}\equiv\epsilon_{x\alpha\beta}[(\mathbf{R}-\mathbf{r}_i)\cdot\mathbf{e}_\alpha][\mathbf{r}_j\cdot\mathbf{e}_\beta]D_{ij}^{-3}. \tag{A2}$$

We use

$$\begin{aligned}&\langle 0,0|F(\mathbf{R},\mathbf{r}_i,\mathbf{r}_j)|i\mu,j\nu\rangle\\&\quad=\langle 0|(\Delta\mathbf{r}_i\cdot\mathbf{e}''_{\mu,i})|i\mu\rangle\langle 0|(\Delta\mathbf{r}_j\cdot\mathbf{e}''_{\nu,j})|j\nu\rangle(\boldsymbol{\nabla}_i\cdot\mathbf{e}''_{\mu,i})\\&\qquad\times(\boldsymbol{\nabla}_j\cdot\mathbf{e}''_{\nu,j})F(\mathbf{R},\mathbf{r}_i,\mathbf{r}_j)\\&\quad=a_a^2(\boldsymbol{\nabla}_i\cdot\mathbf{e}''_{\mu,i})(\boldsymbol{\nabla}_j\cdot e''_{\nu,j})F(\mathbf{R},\mathbf{r}_i,\mathbf{r}_j)\\&\quad\equiv a_a^2\langle F_{\mu\nu;ij}\rangle.\end{aligned} \tag{A3}$$

In this notation

$$E_{IJ}^{(2)}=-2\psi(R_x)a_a^4e^4\sum_{ij}\sum_{\nu,\mu}\langle F_{\mu\nu;ij}^{(1)}\rangle\langle F_{\mu\nu;ij}^{(2)}\rangle(E_\mu+E_\nu)^{-1}. \tag{A4}$$

Then

$$\begin{aligned}\langle F_{\mu\nu;ij}^{(1)}\rangle&=[\mathbf{e}''_{\mu,i}\cdot\boldsymbol{\nabla}_i][\mathbf{e}''_{\nu,j}\cdot\boldsymbol{\nabla}_j]\\&\quad\times\frac{1}{[R^2+r_i^2+r_j^2-2\mathbf{R}\cdot\mathbf{r}_i+2\mathbf{R}\cdot\mathbf{r}_j-2\mathbf{r}_i\cdot\mathbf{r}_j]^{1/2}}\\&=-[\mathbf{e}''_{\mu,i}\cdot\boldsymbol{\nabla}_i][\mathbf{e}''_{\nu,j}\cdot(\mathbf{R}-\mathbf{r}_{ij})]D_{ij}^{-3}\\&=D_{ij}^{-3}\mathbf{e}''_{\mu,i}\cdot\mathbf{e}''_{\nu,j}-3D_{ij}^{-5}[(\mathbf{R}-\mathbf{r}_{ij})\cdot\mathbf{e}''_{\nu,j}]\\&\quad\times[(\mathbf{R}-\mathbf{r}_{ij})\cdot\mathbf{e}''_{\mu,i}].\end{aligned} \tag{A5}$$

Next,

$$\begin{aligned}\langle F_{\mu\nu;ij}^{(2)}\rangle&=[\mathbf{e}''_{\mu,i}\cdot\boldsymbol{\nabla}_i][\mathbf{e}''_{\nu,j}\cdot\boldsymbol{\nabla}_j]\{D_{ij}^{-3}\epsilon_{x\alpha\beta}[(\mathbf{R}-\mathbf{r}_i)\cdot\mathbf{e}_\alpha]\\&\quad\times[\mathbf{r}_j\cdot\mathbf{e}_\beta]\}\\&=[\mathbf{e}''_{\mu,i}\cdot\boldsymbol{\nabla}_i]D_{ij}^{-3}\epsilon_{x\alpha\beta}[(\mathbf{R}-\mathbf{r}_i)\cdot\mathbf{e}_\alpha]\{\mathbf{e}''_{\nu,j}\cdot\mathbf{e}_\beta+3D_{ij}^{-2}\\&\quad\times[\mathbf{r}_j\cdot\mathbf{e}_\beta][\mathbf{e}''_{\nu,j}\cdot(\mathbf{r}_{ij}-\mathbf{R})]\}.\end{aligned} \tag{A6}$$

Thus

$$\begin{aligned}\langle F_{\mu\nu;ij}^{(2)}\rangle&=D_{ij}^{-3}\epsilon_{x\alpha\beta}\{-[\mathbf{e}''_{\mu,i}\cdot\mathbf{e}_\alpha][\mathbf{e}''_{\nu,j}\cdot\mathbf{e}_\beta]+3D_{ij}^{-2}[\mathbf{e}''_{\mu,i}\cdot\mathbf{e}_\alpha]\\&\quad\times[\mathbf{r}_j\cdot\mathbf{e}_\beta][\mathbf{e}''_{\nu,j}\cdot(\mathbf{R}-\mathbf{r}_{ij})]+3D_{ij}^{-2}[(\mathbf{R}-\mathbf{r}_i)\cdot\mathbf{e}_\alpha]\\&\quad\times[\mathbf{r}_j\cdot\mathbf{e}_\beta][\mathbf{e}''_{\nu,j}\cdot\mathbf{e}''_{\mu,i}]+3D_{ij}^{-2}[(\mathbf{R}-\mathbf{r}_i)\cdot\mathbf{e}_\alpha][\mathbf{e}''_{\nu,j}\cdot\mathbf{e}_\beta]\\&\quad\times[(\mathbf{R}-\mathbf{r}_{ij})\cdot\mathbf{e}''_{\mu,i})]-15D_{ij}^{-4}[(\mathbf{R}-\mathbf{r}_i)\cdot\mathbf{e}_\alpha][\mathbf{r}_j\cdot\mathbf{e}_\beta]\\&\quad\times[(\mathbf{R}-\mathbf{r}_{ij})\cdot\mathbf{e}''_{\nu,j}][(\mathbf{R}-\mathbf{r}_{ij})\cdot\mathbf{e}''_{\mu,i})]\}.\end{aligned} \tag{A7}$$

For the helical molecule we may evaluate the above expressions using the explicit relations for the atomic positions given in Eq. (22) and the local coordinate axes given in Eq. (23). In the notation of Eq. (A3), we have

$$E_{IJ}^{(1)}=-2\psi(R_x)e^2\Bigg[a_a^2\sum_{ii'j}\sum_{\mu\mu'\nu}d''_{i\mu}d''_{i'\mu'}F^{(1)}_{\mu\nu;ij}F^{(2)}_{\mu'\nu;i'j}E_\nu^{-1}+\Phi(I\Leftrightarrow J)\Bigg], \tag{A8}$$

where $\Phi(I\Leftrightarrow J)$ designates the corresponding term when molecule $I$ is excited and molecule $J$ is in its ground state.

## APPENDIX B: ISOTROPIC ATOMIC POLARIZABILITY

In this appendix, we analyze the chiral energy when the atomic polarizability is isotropic, so that $E_\nu=E$. Then,

$$E_{IJ}^{(2)}=\psi(R_x)e^4a_a^4\,E^{-1}\sum_{ij}\sum_{\mu\nu}([\boldsymbol{\nabla}_i\cdot\mathbf{e}''_{\mu,i}][\boldsymbol{\nabla}_j\cdot\mathbf{e}''_{\nu,j}]D_{ij}^{-1})\times\epsilon_{x\alpha\beta}\{[\boldsymbol{\nabla}_i\cdot\mathbf{e}''_{\nu,i}][\boldsymbol{\nabla}_j\cdot\mathbf{e}''_{\mu,j}][(\mathbf{R}-\mathbf{r}_i)\cdot\mathbf{e}_\alpha][\mathbf{r}_j\cdot\mathbf{e}_\beta]D_{ij}^{-3}\}. \tag{B1}$$

This can now be evaluated in the space-fixed coordinate system: where, for simplicity, we set $\mathbf{R}=R\mathbf{e}_x$:

$$\begin{aligned}E_{IJ}^{(2)}&=\psi(R_x)e^4a_a^4E^{-1}\sum_{ij}\sum_{\mu\nu}(\nabla_{i,\mu}\nabla_{j,\nu}D_{ij}^{-1})\times(\nabla_{i,\nu}\nabla_{j,\mu}[y_jz_i-y_iz_j]D_{ij}^{-3})\\&\equiv 18\psi(R_x)e^4a_a^4E^{-1}T.\end{aligned} \tag{B2}$$

We have (still in space-fixed coordinates)

$$\begin{aligned}T=&\tfrac{1}{18}\sum_{ij}\sum_{\mu\nu}D_{ij}^{-12}\,[-3D_{ij,\mu}D_{ij,\nu}+\delta_{\mu\nu}D_{ij}^2]\\&\times[-15D_{ij,\mu}D_{ij,\nu}(y_iz_j-y_jz_i)-(3\delta_{\mu z}y_j\\&-3\delta_{\mu y}z_j)D_{ij,\nu}D_{ij}^2+(3\delta_{\nu y}z_i-3\delta_{\nu z}y_i)D_{ij,\mu}D_{ij}^2\\&+(\delta_{\mu z}\delta_{\nu y}-\delta_{\mu y}\delta_{\nu z})]\\=&\sum_{ij}D_{ij}^{-8}(y_jz_i-y_iz_j),\end{aligned} \tag{B3}$$

where $D_{ij}^2=(R-x_{ij})^2+y_{ij}^2+z_{ij}^2$ and

$$\begin{aligned}x_i&=x_i'\cos\alpha_I-\sigma_Iy_i'\sin\alpha_I,\\y_i&=x_i'\sin\alpha_I+\sigma_Iy_i'\cos\alpha_I,\\z_i&=\sigma_Iz_i'.\end{aligned} \tag{B4}$$

First, we analyze this quantity for an arbitrary molecule. Since $T$ depends on the orientations of the two molecules, the pitch is determined by the average of $T$ over orientations. So we consider

$$\langle E_{IJ}^{(2)}\rangle\propto\langle T\rangle\equiv\sum_{\sigma_I\sigma_J}\int d\alpha_I\int d\alpha_JT(\alpha_I\sigma_I;\alpha_J\sigma_J)\times P(\alpha_I,\sigma_I;\alpha_J,\sigma_J). \tag{B5}$$

Following the type of argument used in Ref. [4] it can be shown that this expression does indeed vanish when no molecules are chiral. It is interesting to look at the lowest order terms in the expansion of $\langle T\rangle$ in powers of the transverse coordinates, $x_i$, $y_i$, $x_j$, and $y_j$. The leading term in this expansion is found by setting $D_{ij}^2=R^2+z_{ij}^2$. Then the first-order contribution to $T$ is

$$\begin{aligned}T^{(1)}(\alpha_I\sigma_I;\alpha_J,\sigma_J)=&A_1[\sigma_I\sin\alpha_J-\sigma_J\sin\alpha_I)+A_2[\sigma_J\sin\alpha_J\\&-\sigma_I\sin\alpha_I)+A_3\sigma_I\sigma_J(\cos\alpha_J-\cos\alpha_I)\\&+A_4(\cos\alpha_J-\cos\alpha_I),\end{aligned} \tag{B6}$$

where $A_m=\Sigma_{ij}f_{ij}^{(m)}\Lambda_{ij}^{-4}$, where $\Lambda_{ij}=(R^2+z'^2_i+z'^2_j)^2-4z'^2_iz'^2_j$, and

$$\begin{aligned}f_{ij}^{(1)}&=z_i'x_j'[(R^2+z'^2_i+z'^2_j)^4+24z'^2_iz'^2_j(R^2+z'^2_i+z'^2_j)^2+16z'^4_iz'^4_j],\\f_{ij}^{(2)}&=8z'^2_ix_j'z_j'(R^2+z'^2_i+z'^2_j)[(R^2+z'^2_i+z'^2_j)^2+4z'^2_iz'^2_j],\\f_{ij}^{(3)}&=z_i'y_j'[(R^2+z'^2_i+z'^2_j)^4+24z'^2_iz'^2_j(R^2+z'^2_i+z'^2_j)^2+16z'^4_iz'^4_j],\\f_{ij}^{(4)}&=8z'^2_iy_j'z_j'(R^2+z'^2_i+z'^2_j)[(R^2+z'^2_i+z'^2_j)^2+4z'^2_iz'^2_j].\end{aligned} \tag{B7}$$

As discussed in Appendix C, the distribution function $P$ for nematics involves only net even powers of sines and cosines, so that, a nonzero result for $\langle T\rangle$ can only result if chiral contributions to $P$ are included. Actually, this condition is required, because it is clear that achiral molecules can have nonzero values of the $f$'s. Traditionally, no consideration is given to the role of chiral biaxial correlations as a mechanism for cholesteric pitch, although these must be included for a fully consistent calculation [4].

At second order in the transverse coordinates we evaluate $T$ with $D_{ij}^2=R^2-2Rx_{ij}+z_{ij}^2$. Thereby, we find a second-order contribution to $T$ of

$$\begin{aligned}T^{(2)}(\alpha_I,\sigma_I;\alpha_J,\sigma_J)=&B_1(\sigma)\cos\alpha_I\cos\alpha_J+B_2(\sigma)\sin\alpha_I\sin\alpha_J\\&+B_3[\cos(2\alpha_I)+\cos(2\alpha_J)]+\cdots,\end{aligned} \tag{B8}$$

where $\cdots$ indicates terms that change sign when either both $\sin\alpha$'s change sign or when both $\cos\alpha$'s change sign. [These terms do not survive the average in Eq. (B5) when $P$ has nematic symmetry.] Also in Eq. (B8) $\sigma\equiv\sigma_I\sigma_J$ and

$$B_1(\sigma)=16R\sum_{ij}x_i'z_i'y_j'\sigma D_0^{-10},$$

$$B_2(\sigma) = -16R\sum_{ij} x_i' y_j' z_j' D_0^{-10}, \tag{B9}$$

$$B_3(\sigma) = -8R\sum_{ij} x_i' y_i' z_j' \sigma D_0^{-10},$$

where $D_0^2 = R^2 + z_i'^2 + z_j'^2 - 2\sigma z_i' z_j'$. Note that these quantities which do survive the average of Eq. (B5) must vanish for achiral molecules. (Because of our choice of principal axes [15], if a molecule is achiral, it has a mirror plane perpendicular to one of the principal axes directions.) Generically, the nonvanishing of one or more sums in Eq. (B9) is equivalent to the nonvanishing of $\Sigma_i x_i' y_i' z_i'$. For instance, for the ''twisted H'' molecule invoked in Refs. [4] and [3] one sees that the three two-fold rotation axes ensure that $B_1(\sigma) = B_2(\sigma) = 0$, but $B_3(\sigma)$ is nonzero and is given by

$$B_3(\sigma) = -8R\sum_{ij} \Lambda_{ij}^{-5} x_i' y_i' z_i' z_j'^2 [10(R^2 + z_i'^2 + z_j'^2)^4 + 80(R^2 + z_i'^2 + z_j'^2)^2 z_i'^2 z_j'^2 + 32 z_i'^4 z_j'^4]. \tag{B10}$$

One sees the appearance of the quantity $x_i' y_i' z_i'$, which is characteristic of a chiral molecule [4].

For the helical molecule, we have

$$T = 12a\rho^2 \int_{-L/2}^{L/2} dz \int_{-L/2}^{L/2} dz' D^{-8} [\sin(qz + \alpha_I) z' - \sin(qz' + \alpha_J) z], \tag{B11}$$

where $\rho$ is the density of atoms ($\rho = N_a/L$) and

$$D^2 = R^2 - 2Ra[\cos(qz + \alpha_I) - \cos(qz' + \alpha_J)] + 2a^2 - 2a^2 \cos(qz - qz' + \alpha_I - \alpha_J) + z^2 + z'^2 - 2zz'. \tag{B12}$$

## APPENDIX C: SYMMETRY OF ORIENTATIONAL CORRELATION FUNCTION

In this appendix, we give a brief discussion of the symmetry of distribution function $P_\alpha(\alpha_I, \sigma_I; \alpha_J, \sigma_J)$ for the orientations of two molecules both of whose centers lie in a plane perpendicular to the director **n**. We assume a nematic phase with no long range biaxial order. Therefore, the only vector needed to describe the nematic phase is the director **n** and we have invariance under $\mathbf{n} \to -\mathbf{n}$. This distribution function must be constructed from the available vectors in the problem, which we may take to be

$$\mathbf{e}_{x,I}', \quad \mathbf{e}_{z,I}', \quad \mathbf{e}_{x,J}', \quad \mathbf{e}_{z,J}', \quad \mathbf{R}, \quad \mathbf{n}, \tag{C1}$$

where **R** is the intermolecular displacement vector. Such invariants, to be consistent with the nematic phase should not involve cross products. Thus, we may utilize

$$(\mathbf{e}_{x,I}' \cdot \mathbf{e}_{x,J}'), \ (\mathbf{e}_{z,I}' \cdot \mathbf{e}_{z,J}'), \ (\mathbf{e}_{z,I}' \cdot \mathbf{n}), \ (\mathbf{e}_{z,J}' \cdot \mathbf{n}), \ (\mathbf{e}_{x,I}' \cdot \mathbf{R}), \ (\mathbf{e}_{x,J}' \cdot \mathbf{R}), \tag{C2}$$

where the nematic director is along $\mathbf{e}_z$. Since the expression must be invariant under change of sign of **n**, we cannot invoke the factor $F \equiv (\mathbf{e}_{z,I}' \cdot \mathbf{n})^p (\mathbf{e}_{z,J}' \cdot \mathbf{n})^q$, with $p+q$ odd. Also note that $\mathbf{e}_{z,I}'$ and $\mathbf{e}_{z,J}'$ are both collinear to **n**. Therefore a factor like $F$ is equivalent to unity or $(\mathbf{e}_{z,I}' \cdot \mathbf{e}_{z,J}')$. Thus, we may take our list of invariants to be

$$(\mathbf{e}_{x,I}' \cdot \mathbf{e}_{x,J}'), \ (\mathbf{e}_{z,I}' \cdot \mathbf{e}_{z,J}'), \ (\mathbf{e}_{x,I}' \cdot \mathbf{R}), \ (\mathbf{e}_{x,J}' \cdot \mathbf{R}), \tag{C3}$$

which are, respectively

$$\cos(\alpha_I - \alpha_J), \ \sigma_I \sigma_J, \ (X\cos\alpha_I + Y\sin\alpha_I), \ (X\cos\alpha_J + Y\sin\alpha_J). \tag{C4}$$

So we write $P_\alpha$ as

$$P_\alpha(\alpha_I, \sigma_I; \alpha_J, \sigma_J) = \sum_{\not{}mn} [A(R^2)_{\not{}mn} + B(R^2)_{\not{}mn}\sigma_I\sigma_J] \times \cos^{\not{}}(\alpha_I - \alpha_J)(X\cos\alpha_I + Y\sin\alpha_I)^m (X\cos\alpha_J + Y\sin\alpha_J)^n, \tag{C5}$$

where $R^2 = X^2 + Y^2$. One can see that this is an invariant against rotation, by noting that rotation by $\pi$ about the $x$ axis (which is the direction of the chiral wave vector) takes $Y$ into $-Y$, and changes the signs of the $\alpha$'s and $\sigma$'s. Rotation by $\pi$ about the $z$ axis changes the sign of **R** and adds $\pi$ to the $\alpha$'s. Now we set $Y = 0$. Using $\cos(\alpha_I - \alpha_J) = \cos\alpha_I \cos\alpha_J + \sin\alpha_I \sin\alpha_J$ and $\cos^2\alpha = 1 - \sin^2\alpha$, we can write the result in the form

$$P_\alpha(\alpha_I, \sigma_I; \alpha_J, \sigma_J) = \sum_{k\not{}mn} [C(R^2)_{k\not{}mn} + D(R^2)_{k\not{}mn}\sigma_I\sigma_J] \times (\sin\alpha_I)^k (\sin\alpha_J)^{\not{}} (X\cos\alpha_I)^m (X\cos\alpha_J)^n, \tag{C6}$$

where $k + \not{}$ is restricted to be even. A symmetry we have *not* yet used is that molecules $I$ and $J$ are identical. Thus, we have the symmetry operation $\mathbf{R} \to -\mathbf{R}$ and $I$ and $J$ are interchanged. This tells us that

$$C(R^2)_{k\not{}mn} = C(R^2)_{\not{}knm}(-1)^{m+n}, \quad D(R^2)_{k\not{}mn} = D(R^2)_{\not{}knm}(-1)^{m+n}. \tag{C7}$$

Now, consider the restriction imposed by requiring that the constituent molecules actually be achiral. Let us suppose that the molecules have a mirror plane perpendicular to the body $x$ axis. We can relate an arbitrary initial configuration, shown in the left panel of Fig. 11 to the configuration we obtain by a reflection taking $\mathbf{e}_y$ into $-\mathbf{e}_y$, as shown in the right-hand panel. This mirror operation, which changes the sign of $\cos\alpha_I$ and that of $\cos\alpha_J$, is supposed to leave $P_\alpha$ invariant. This implies that in Eq. (C6), $m+n$ must be even. The conclusion is that for a nematic all of whose molecules are identical, the orientation correlation function for molecules in the same equatorial plane must be of the form

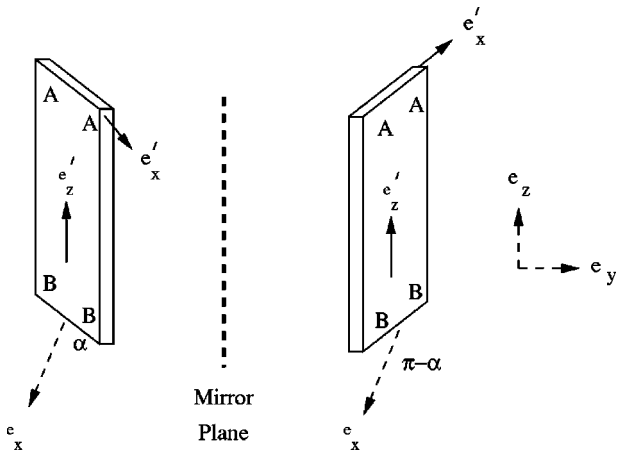


FIG. 11. Left: orientation with $\sigma=+1$ and nonzero $\alpha$. Right: orientation after mirror operation taking $\mathbf{e}_y$ into $-\mathbf{e}_y$.

$$P_\alpha(\alpha_I,\sigma_I;\alpha_J,\sigma_J) = \sum_{jkmn}[C(R^2)_{k\not{m}n}+D(R^2)_{k\not{m}n}\sigma_I\sigma_J] \times(\sin\alpha_I)^k(\sin\alpha_J)^{\not{m}}(\cos\alpha_I)^m(\cos\alpha_J)^n, \tag{C8}$$

where $k+\not{m}$ and $m+n$ are even.

A similar discussion can be given for the case when the molecules are achiral by virtue of having a mirror plane perpendicular to $\mathbf{e}'_y$ or $\mathbf{e}'_z$. In any case, we still arrive at the additional constraint that $m+n$ is even. We could have based the discussion on the vectors $\mathbf{e}'_{y,I}$ and $\mathbf{e}'_{y,J}$ instead of $\mathbf{e}'_{x,I}$ and $\mathbf{e}'_{x,J}$. The construction of proper rotational invariants would then lead to the condition that $m+n$ be even. The additional constraint caused by requiring the constituent molecules to be achiral would then lead to the condition that $k+\not{m}$ be even. So, the discussion given above can be extended to cover the most general case of a nematic, which perforce must consist of achiral molecules.

## APPENDIX D: OSCILLATORY DEPENDENCE ON MOLECULAR LENGTH

In this appendix, we study the dependence of the twist energy $E_{IJ}^{(2)}$ on the molecular length $L$. We will show that in the limit of large $L$, $E_{IJ}^{(2)}$ has significant end effects which cause it *not* to be simply a function of $\alpha_1-\alpha_2$. To obtain clear analytic results we will assume the polarizability to be isotropic ($\delta=\eta=0$) and will work within the expansion in powers of the transverse coordinates. In other words, we will treat the helical molecule with $a/R\ll 1$.

At first order in the transverse coordinate (a) we have [in the notation of Eq. (B2)] that $T=T_1$, where

$$T_1=a\rho^2\int_{-L/2}^{L/2}dz_1\int_{-L/2}^{L/2}dz_2\frac{z_1\sin(qz_2+\alpha_J)-z_2\sin(qz_1+\alpha_I)}{[R^2+(z_1-z_2)^2]^4} \tag{D1}$$

so that

$$T_1=T_{1a}(\cos\alpha_J-\cos\alpha_I), \tag{D2}$$

where

$$T_{1a}=a\rho^2\int_{-L/2}^{L/2}dz_1\int_{-L/2}^{L/2}dz_2\frac{z_1\sin(qz_2)}{[R^2+(z_1-z_2)^2]^4}. \tag{D3}$$

We do not pursue evaluation of this term any further because the $\alpha$ dependence of this result gives a vanishing contribution to $\langle E\rangle$, when it is averaged over an orientational probability distribution consistent with nematic symmetry.

At second order in $a$ we have $T=T_2$, where

$$T_2=Ra^2\rho^2\int_{-L/2}^{L/2}dz_1\int_{-L/2}^{L/2}dz_2 \times\frac{z_1\sin(qz_2+\alpha_J)-z_2\sin(qz_1+\alpha_I)}{[R^2+(z_1-z_2)^2]^5}\,8[\cos(qz_1+\alpha_I) -\cos(qz_2+\alpha_J)], \tag{D4}$$

so that

$$T_2=U\cos(\alpha_I-\alpha_J)+V\cos(\alpha_I+\alpha_J)+W\cos(2\alpha_I) +W\cos(2\alpha_J), \tag{D5}$$

where

$$U=8Ra^2\rho^2\int_{-L/2}^{L/2}s\,ds\int_{-L/2}^{L/2}dt\frac{\sin[q(t-s)]}{[R^2+(s-t)^2]^5} =8Ra^2\rho^2\int_{-L/2}^{L/2}s\,dsG_5(s)\equiv 8Ra^2\rho^2u, \tag{D6}$$

$$V=8Ra^2\rho^2\int_{-L/2}^{L/2}s\,ds\int_{-L/2}^{L/2}dt\frac{\sin[q(t+s)]}{[R^2+(s-t)^2]^5} =8Ra^2\rho^2\int_{-L/2}^{L/2}s[\cos(2qs)G_5(s)+\sin(2qs)H_5(s)]ds \equiv 8Ra^2\rho^2v, \tag{D7}$$

and

$$W=-4Ra^2\rho^2\int_{-L/2}^{L/2}ds\sin(2qs)[sF_1(s)+F_2(s)] \equiv 4Ra^2\rho^2w, \tag{D8}$$

where

$$F_1(s)=\int_{-L/2-s}^{L/2-s}\frac{du}{(R^2+u^2)^5}, \tag{D9}$$

$$F_2(s)=\int_{-L/2-s}^{L/2-s}\frac{u\,du}{(R^2+u^2)^5}, \tag{D10}$$

$$G_p(s)=\int_{-L/2-s}^{L/2-s}\frac{\sin qt}{(R^2+t^2)^p}dt, \tag{D11}$$

and

$$H_p(s)=\int_{-L/2-s}^{L/2-s}\frac{\cos qt}{(R^2+t^2)^p}dt. \tag{D12}$$

After considerable algebra, we obtained the following results for large $L/R$:

$$u=J_4(q)-R^2J_5(q)-\tfrac{1}{8}(qL)I_4(q), \tag{D13a}$$

$$\begin{aligned}v=&-(L/q)I_5(q)\cos(qL)-\tfrac{1}{2}(L/q)J_5(q)\sin(qL)+\cos(qL)\\&\times[-\tfrac{1}{8}J_4(q)-q^{-2}J_5(q)+(8qR^8)^{-1}]\\&+\sin(qL)[\tfrac{1}{8}I_4(q)+q^{-2}I_5(q)],\end{aligned} \tag{D13b}$$

$$\begin{aligned}w=&[-\tfrac{1}{2}C_5R^{-9}-\tfrac{1}{2}I_5(2q)](L/q)\cos(qL)-\tfrac{1}{2}J_5(2q)\\&\times(L/q)\sin(qL)+\cos(qL)\left[(8qR^8)^{-1}-\frac{1}{2q^2}J_5(2q)\right]\\&+\sin(qL)\left[C_5(2q^2R^9)^{-1}+\frac{1}{2q^2}I_5(2q)\right],\end{aligned} \tag{D13c}$$

where

$$I_p(q)=\int_0^\infty\frac{\cos qu}{(R^2+u^2)^p}du,$$

$$J_p(q)=\int_0^\infty\frac{\sin qu}{(R^2+u^2)^p}du, \tag{D14}$$

$$C_p=\int_0^\infty\frac{dx}{(1+x^2)^p}.$$

The main approximation in our results is that integrals with integrands as in $I_p$ and $J_p$ which have upper limits $L/2$ or $L$ are replaced by the integrals written in Eq. (D14) with an upper limit of $\infty$. One has the results

$$I_4(q)=\frac{\pi q^3e^{-qR}}{96R^4}[1+6/(qR)+15/(qR)^2+15/(qR)^3], \tag{D15}$$

$$\begin{aligned}I_5(q)=&\frac{\pi q^4e^{-qR}}{768R^5}[1+10/(qR)+45/(qR)^2+105/(qR)^3\\&+105/(qR)^4],\end{aligned} \tag{D16}$$

$$J_p(q)=\frac{1}{qR^{2p}}[1+2p(qR)^{-2}+12p(p+1)(qR)^{-4}+\cdots], \tag{D17}$$

where the result for $J_p$ is an asymptotic expansion for $qR\gg1$. We compared these results with exact numerical evaluations of $E_{IJ}^{(2)}$ and found very close agreement.

We see from Eq. (D13) that in the large $L$ limit, the quantities $V/L$ and $W/L$ have oscillatory contributions, which are of the same order as the large $L$ limit of $U/L$.


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